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Interactions between Sodium polyacrylate and Mixed Surfactants of Polyoxyethylene tert-octyl phenyl ether and Dodecyltrimethylammonium bromide

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Abstract

The interactions between sodium polyacrylate (PANa) and mixed surfactants of polyoxyethylene tert-octyl phenyl ether (TX100) and dodecyltrimethylammonium bromide (DTAB) in 40 mM NaBr aqueous solutions were studied by isothermal titration calorimetry (ITC). It was found that whatever DTAB titrated into PANa/TX100 or TX100/DTAB titrated into PANa, three endothermic peaks were detected; representing three processes: (1) binding of DTAB monomers to PANa chains through electrostatic interaction, (2) polymer-induced micellization, and (3) cross-linking of polymer chains. The interaction mechanism was interpreted by a thermodynamic model, and it was found that when the molar ratio of bound DTAB to the carboxylate group of the polymer ($C_{\mathrm{DTAB}}^{\mathrm{poly}}/C_{\mathrm{poly}}$) reached about 0.5, the polymer-induced micellization occurred; while $C_{\mathrm{DTAB}}^{\mathrm{poly}}/C_{\mathrm{poly}}$ reached about 1, indicating the complete neutralization of the electrostatic charges on the polymer chains, the cross-linking of polymer chains started and precipitation was observed; finally, as $C_{\mathrm{DTAB}}^{\mathrm{poly}}/C_{\mathrm{poly}}$ reached 1.3, precipitation was redissolved slowly due to reversion of the charge ratio on the polymer chains.

Keywords: polyacrylate, mixed surfactants, isothermal titration calorimetry, thermodynamic model

1. Introduction

A large number of researchers have devoted their attentions to polymer-surfactant systems in recent decades[1-10] because of their importance in the scientific interests and practical applications in biochemical and pharmaceutical products, paint, cosmetic, and other industry fields. Interaction of surfactant with oppositely charged linear polyions may result in a cooperative process above its aggregation concentration (cac) that is 1-3 order of magnitude lower than the critical micelle concentration (cmc). This aggregation occurs through the binding of the surfactant onto the polymer chains and the binding behavior is usually affected by the polyelectrolyte structure,[11-14] the surfactant property,[8, 15, 16] and the solvent medium,[9, 17] etc. It is generally accepted that the main interaction between polyelectrolyte and oppositely charged surfactant is predominantly governed by the electrostatic force; however it may be reinforced by hydrophobic force between bound surfactant molecules.

The interactions between the polyelectrolyte and mixed surfactants have also been studied,[18-36] most of which involved the system of poly(diallyldimethylammonium chloride) (PDDAC) and mixed surfactants of polyoxyethylene tert-octyl phenyl ether

(TX100) and sodium dodecyl sulfate (SDS).[18-20, 22-24, 26-29, 32, 33] It was found in those studies that polyelectrolyte/surfactants interactions and the phase behavior were mainly determined by the ionic strength and the composition of the mixed surfactants, not by the concentration of polymer or total surfactant.

Many different techniques have been used to study the interactions and the phase behaviors of polymer/mixed surfactants systems, such as ultrafiltration,[20] turbidimetric,[18-22, 24, 26, 28, 31-34] light scattering (QELS),[19, 20, 23-28, 31-33, 35] potentiomeric titration,[22] calorimetry,[29, 36] deuterium NMR spectroscopy,[30] electrophoresis,[31-34] fluorescence,[34] electron spin resonance (ESR),[35] and electron microscopy.[36] The isothermal titration calorimetry (ITC) is a sensitive technique and has an advantage that not only the interactions between polymer and surfactant but also the phase behaviors of the polymer/surfactant systems can be investigated simultaneously. The calorimetric studies can also give the corresponding thermodynamic parameters such as various critical concentrations, and the changes of the enthalpy (ΔH), entropy (ΔS) and Gibbs energy (ΔG) in various phase transitions which are crucial to understanding the interaction of polymer/surfactant. However, to the best of our knowledge, the study of the interactions between polyelectrolytes and mixed surfactants by ITC is very seldom,[36] and thus more detailed ITC works are helpful to fully disclose the interactions between polyelectrolyte and mixed micelles.

Poly(acrylic acid) (PAA) is a weak polyelectrolyte, and has surprisingly strong affinity with cationic surfactants. The system of PAA/cationic surfactant has potential applications such as control of drug delivery, chemical reactivity, and nonspecific binding of DNA with basic protein, and may be used as a simplified model for elucidating the behavior of biological systems.[37, 38] We studied the interactions between sodium polyacrylate (PANa) and anion-cation mixed surfactants of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and dodecyltrimethylammonium bromide (DTAB) in 40 mM NaBr solution previously.[36] It was found that the interaction mechanism varied with the titration order. When DTAB titrated into PANa/AOT, DTAB micelles dissociated into monomers first, then the monomers bind to PANa/AOT complex; whereas AOT/DTAB mixed micelles bind to PANa when AOT/DTAB titrated into PANa. This variation of the interaction mechanism with the titration order was attributed to formation of DTAB-rich AOT/DTAB mixed micelle in the low surfactant concentration region for the titation of AOT/DTAB into PANa.[36] It is interesting to inverstigate the polymer/mixed surfactants interactions for the similar system with AOT being replaced by non ionic surfactant TX100, which has smaller cmc value than AOT, hence possibly forms the TX100-rich TX100/DTAB micelle.

In this paper, we study the interaction between PANa and the nonionic/cationic mixed surfactants TX100/DTAB using ITC at low ionic strength. Two types of titration experiments are performed in order to investigate the effect of the mixing order on the interaction mechanism. Detailed information on enthalpy changes is further analyzed by a thermodynamic model to investigate the mechanism of adsorption of surfactants on the polyelectrolyte chains.

2. Experimental section

2.1. Materials

The polyelectrolyte used in this study was poly(acrylic acid) (PAA, 25% solution from Alfa Aesar Chemical Co.), which had an approximate average molecular weight of 2.58×10^5 determined by static light scattering measurements in our laboratory. The cationic surfactant and nonionic surfactant were dodecyltrimethylammonium bromide (DTAB, from J&K chemical LTD, ≥99% mass fraction) and polyoxyethylene tert-octyl phenyl ether (TX100, Fluka, $n_D^{20} = 1.490 - 1.494$), respectively. Sodium bromide (NaBr, ≥99.0% mass fraction) and Sodium hydroxide (NaOH, ≥96% mass fraction) were purchased from Sitong Chemical Company (Tianjin, China) and Tianjin Chemical Company (Tianjin, China), respectively. All materials were used without further purification. Twice distilled water was used in preparations of the samples.

2.2. Preparation of polyelectrolyte solutions

Sodium polyacrylate (PANa) was obtained by adding an appropriate amount of NaOH to poly(acrylic acid) aqueous solution. Then NaBr was added, and the solution was diluted with water and stirred rigorously. Finally, more NaOH was added to adjust pH of the PANa/NaBr solution to a value larger than 9 (about 9.5) to ensure almost complete ionization of PANa.[39, 40] The aim of addition of NaBr was to weaken the interaction between PANa and DTAB to obtain more detailed interaction information. The concentrations of the carboxylate groups and NaBr in the solutions were 6.93 mM and 40 mM, respectively.

2.3. Isothermal titration microcalorimetry (ITC)

The isothermal titration data were collected by using the TAM 2277-201 microcalorimetric system (Thermometric AB, Järfäfla, Sweden), which has 4 mL sample and reference cells. In study of the interactions between polyelectrolyte and mixed surfactants, the titrations were carried out in two ways. In “type I” titrations, DTAB aqueous solution was added to 2.2 mL NaBr solution containing different TX100 concentrations with or without PANa. “Type II” titration corresponds to the addition of TX100/DTAB mixed micelles with a certain molar ratios of TX100 to DTAB into 2.2 mL NaBr solution with or without PANa. The stirring speed in the sample cell was set at 60 rpm, and the experiment temperature was 25.00 ± 0.02 ^{o}C. The values of the observed differential enthalpy (ΔH_{obs}) for various concentrations of surfactants were obtained by the integral of the areas under the calorimetric peaks, and normalized by the small amounts of injected surfactants. The uncertainty in measurement of ΔH_{obs} for an individual titration process was about 0.05 kJ/mol. Each of titration experiments was carried out twice; the reproducibility is reported in section 3.2. The enthalpy curves without PANa are named as the background curves in this paper, while the ones with PANa are named as the binding curves.

3. Results and discussion

3.1. Interaction between PANa and TX100

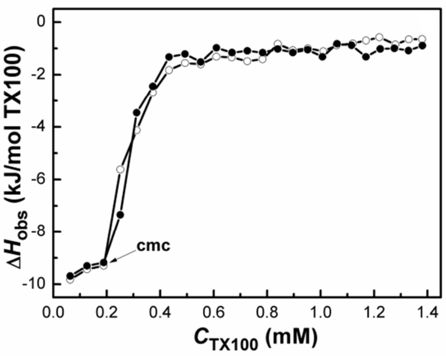

Figure 1. Observed differential enthalpy for titrating 14 mM TX100 into NaBr and PANa/NaBr aqueous solutions: (○) NaBr solution, (●) PANa in NaBr aqueous solution.

The plots of the observed differential enthalpy ΔH_{obs} vs. the concentration of surfactant for titrating 14 mM TX100 into 40 mM NaBr aqueous solutions with or without PANa are shown in Figure 1. The background curve denoted by blank circles has a sigmoid shape with abrupt change which corresponds to the micelle formation. The critical micelle concentration (cmc) was identified by the intersection of extrapolated lines of the initial portion and the rapidly decreasing portion of the curves. Meanwhile, the enthalpy of the micellization (ΔH_{mic}) was determined from the difference of the ΔH_{obs} between the two linear segments of the plot at the cmc.[41, 42] It was found that the values of cmc and ΔH_{mic} were 0.19 mM and 8.02 kJ/mol, respectively; which were both smaller than 2.3 mM determined by Majhi[43] and 12.2 kJ/mol determined by Sharma[44] in TX100 aqueous solutions. These differences may be resulted from the addition of NaBr in our experiment. The electrolyte NaBr disrupts hydrogen bonds between ethylene oxide (EO) groups and H_2O in the solution, leading to dehydration and contraction of the TX100 monomer chains, which is in favor of micelle formation and hence decreases the values of cmc and ΔH_{mic}. The cmc of TX100 is nearly a thirtieth of that for DTAB (5.91 mM).[36] It may be attributed to that the hydrophobility of TX100 is stronger than DTAB, and no electrostatic repulsion exists on the TX100 micelle surface, thus TX100 is much easier to form micelle than DTAB.

When TX100 was added into the PANa solution (indicated by filled circles in Figure 1), it was found that the binding enthalpy curve coincides with the TX100 background curve, and the cmc value of TX100 is not affected by PANa; indicating that the interaction of TX100 and PANa in the system is negligible. Our result is consistent with reference,[21] it was found that poly(acrylic acid) could form complexes with TX100 by H bonding only for pH below 5, while the H bonding was suppressed as pH increases; and no interaction between TX100 and PANa was detected for pH being about 9.5 in this system.

3.2. Interactions between PANa and TX00/DTAB mixed surfactants

The studies of interactions between PANa and mixed surfactants were performed in two ways. In type I titrations, 70 mM DTAB was added to the TX100 solutions or PANa/TX100 solutions in 40 mM NaBr, where the initial concentrations of TX100 (C^{0}_{TX100}) in ampoule were 5.6 mM, 14 mM, and 28 mM, respectively. The plots of ΔH_{obs} vs. DTAB concentration (C_{DTAB}) are shown in Figures 2a, 2b and 2c. Figure 2d shows the phase behaviors of polymer/surfactant solutions with various DTAB concentrations denoted by letters corresponding to those in Figure 2b. As an example, in Figure 2a, we present the reproducibility of two measurements, where it can be seen that two curves from two independent titrations are well consistent with each other and three peaks are well reproducible. In "type II" titrations, PANa solutions were titrated by TX100/DTAB mixed micelles, in which the concentration of DTAB was 70 mM, while the concentration of TX100 was 5.6 mM, 14 mM and 28 mM for each of the three individual titrations, respectively. The plots of ΔH_{obs} vs. the total concentration of the surfactant (C_{st}) are shown in Figures 3a, 3b and 3c, and Figure 3d shows the phase behaviors of polymer/surfactant solutions with various surfactant concentrations denoted by letters corresponding to those in Figure 3b. Although peaks A and B in Figures 3 are somewhat smaller as compared with that in Figure 2, the heights of them are larger than 8 times of estimated uncertainties.

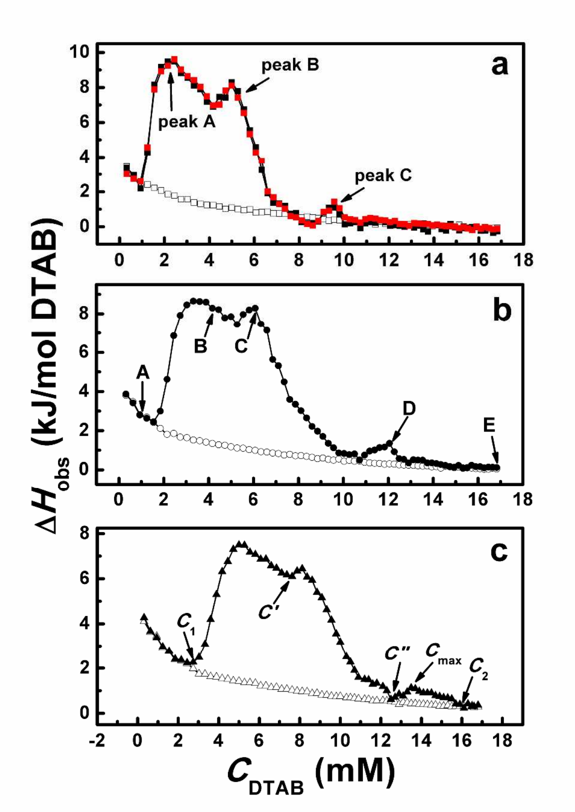

Figure 2. Observed differential enthalpy for titrating 70 mM DTAB into TX100/NaBr and PANa/TX100/NaBr aqueous solutions with different TX100 concentrations. (a) C^0_{TX100}=5.6 mM: (□) background curve (■) binding curve: first measurement (black), second measurement (red); (b) C^0_{TX100}=14 mM: (○) background curve (●) binding curve, the locations denoted by letters A, B, C, D, E are discussed in the text; (c) C^0_{TX100}=28 mM: (Δ) background curve (▲) binding curve. (d) The phase behaviors of polymer/surfactant solutions denoted by letters A, B, C, D, E are corresponding to those in (b).

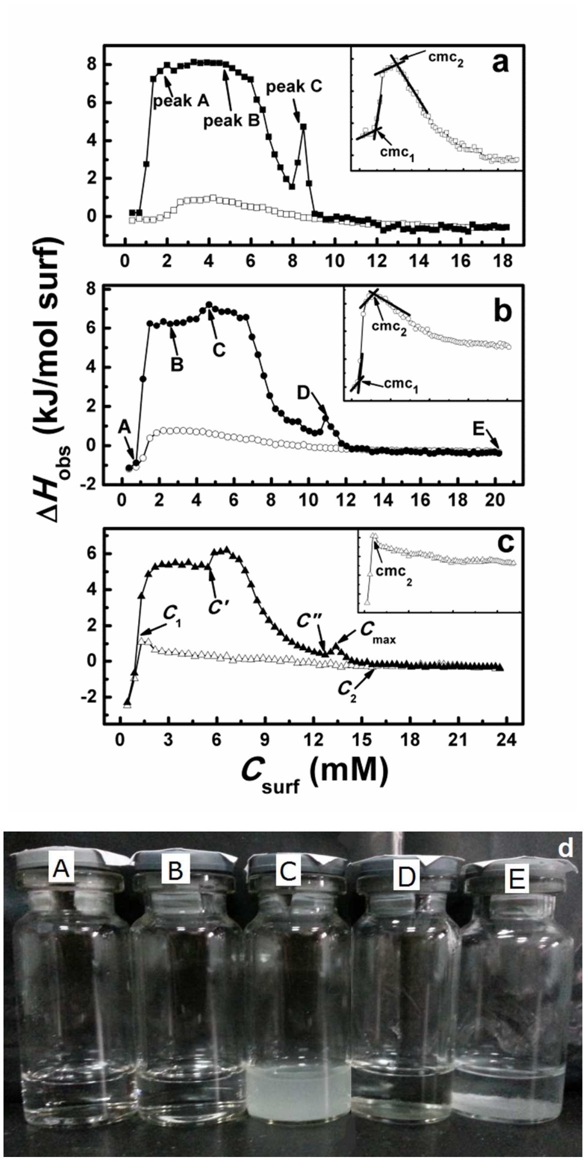

Figure 3. Observed differential enthalpy for titrating TX100/DTAB mixed micelles into NaBr and PANa/NaBr aqueous solutions. The mixed micelles have the molar ratios of C_{TX00}:C_{DTAB}: (a) 5.6:70 (□) background curve, (■) binding curve; (b) 14:70 (○) background curve (●) binding curve; the locations denoted by letters A, B, C, D, E are discussed in the text; (c) 28:70 (Δ) background curve, (▲) binding curve. Insets show magnified views of the background curves. (d) The phase behaviors of polymer/surfactant solutions denoted by letters A, B, C, D, E are corresponds to those

in (b).

3.2.1. Background curves

As shown in Figure 2, in “type I” titration, the three background curves denoted by the blank symbols show that ΔH_{obs} generally decreases with the increase of the DTAB concentration. The concentrations of TX100 in the sample cells for the three titrations are all above its cmc value in 40 mM NaBr aqueous solutions, thus TX100 micelles and TX100 monomers are coexistent in the solutions. When DTAB micelles are added into the solutions, the DTAB micelles disassociate into monomers, and then a part of monomers enter the TX100 micelles and form TX100-rich mixed micelles.

As shown in the inserts of Figure 3, in “type II” titration, the shape of the left part of each of the three background curves is similar to that of the pure TX100; while the right part of enthalpy curve is similar to that of pure DTAB, indicating that the TX100-rich mixed micelles or pure TX100 micelles form first, then transform to DTAB-rich mixed micelles.

It may be observed from the inserts of Figures 3a and 3b that the increase rates of ΔH_{obs} with C_{surf} abruptly change in the initiate parts of the two titration curves with the molar ratios of TX100 to DTAB being 5.6:70 and 14:7. The points corresponding to the abrupt changes are determined as first critical micelle concentrations (cmc_1) denoted in the inserts, indicating the formation of the TX100-rich mixed micelles. However, for the sample with the molar ratio of TX100 to DTAB being 28:70, no such change of the increases rate is observed (see the insert of Figures 3c), which is possibly resulted from that the mixed micelle is formed at very low concentration i.e.

cmc_1 is even smaller than the concentration of 0.42 mM at the first titration point. The enthalpies for the three systems decrease after certain total surfactant concentrations, which are defined as the second critical micelle concentrations (cmc_2) and indicate the transformations to DTAB-rich mixed micelles. The values of cmc_1 and cmc_2 are listed in Table 1. Our results are consistent with that of Cui et al,[45] who studied the ionic/nonionic mixed systems (12-2-12/TX100, 14-2-14/TX100, and SDS/TX100) and ionic/ionic mixed systems (12-2-12/TTAB, 14-2-14/TTAB, and SDS/CTAB) in heavy water solutions by ^{1}H NMR spectroscopy. They found that the component with lower cmc in the mixed solutions aggregated first; then the other one entered the aggregates as the total surfactant concentration increased, resulting in the mixed micelles.

The dependence of the critical concentration C_m of an ideal mixture of two surfactants on their individual critical concentrations C_m1 and C_m2 of the two pure surfactants can be expressed in terms of the Clint's equation [46]

$$\frac{1}{C_\mathrm{m}} = \frac{\alpha}{C_\mathrm{m1}} + \frac{1-\alpha}{C_\mathrm{m2}} \qquad (1)$$

where α is the mole fraction of TX100 in the solution. The values of C_m for the mixed surfactants TX100/DTAB were calculated by Eq. (1) and are compared with the measured values of cmc_1 in Table 1. As shown in Table 1, all the three values of cmc_1 are smaller than the values of C_m calculated through the Clint's equation, indicating attractive interactions between the two surfactants and negative deviations from the ideal mixing behavior in the mixed micelles. The values of cmc_1 and cmc_2 decrease with the molar ratio of TX100 to DTAB, which may be attributed to the decrease of the electrostatic repulsion between the surfactant headgroups by mixing the charged surfactant with the non-ionic surfactant and hence stabilizing the micelles,[47] since EO group of TX100 has a negligible contribution to the interaction between cationic surfactant DTAB and nonionic surfactant TX100 in the surfactant mixtures.[48]

Table 1. Values of cmc for TX100/DTAB mixed surfactant systems at 298.15 K

C_{TX100}(mM):C_{DTAB}(mM)	C_{m} (mM)	cmc$_1$ (mM)	cmc$_2$ (mM)
5.6:70	1.82	1.17	4.20
14:70	0.98	0.87	2.93
28:70	0.61	< 0.42	1.67

3.2.2. Binding curves

From Figures 2 and 3, whatever for “type I” or “type II” titration, it may be found that each of the three binding curves exhibit three endothermic peaks A, B, and C (denoted only in Figures 2a and 3a) and five critical points C_1, C', C'', C_{max} and C_2 (denoted only in Figures 2c and 3c). It is known from above results that the interaction of TX100 and PANa is ignorable. At low surfactant concentration, each of the binding curves coincides with the background one, indicating that the added DTAB also does not interact with the polymer; thus the endothermic titration heat effect is resulted only from dissociation of the micelles, dilution of the dissociated surfactant monomers, and the interaction between surfactants. As the surfactant concentration increases to C_1, the solution is still transparent (see the bottle A in

Figures 2d or 3d), but the binding curve starts to deviate from the background one, which indicates that DTAB monomers bind to the anionic sites of the polymer chains mainly by electrostatic interaction to yield an additional endothermic heat effect and further to form peak A. The solution becomes slight milk-white (see the bottle B in Figures 2 or 3). The value of ΔH_{obs} increases rapidly again when the concentration reaches C' to form peak B; in this region, the neighborly bound DTAB molecules start to aggregate through hydrophobic interaction and form the PANa/DTAB micelles,[40] and the solution becomes milk-white (see the bottle C in Figures 2 or 3). Although the bulk concentration of DTAB at C' is below the cmc of DTAB in the solution without polymer, the local concentration of DTAB on the polymer chains is high enough to induce the micellization. When surfactant concentration reaches C'', the enthalpy increases again to form peak C, where the TX100/DTAB mixed micelles are possibly linked by different polymer chains[49] to induce the polymer cross-linking; some small precipitates appear at the bottom of the bottle (see the bottle D in Figures 2 or 3). With further increase of the surfactant, the enthalpy curve levels off; in this stage, the opaque solution becomes clear, however precipitation is observed. For DTAB titrated into PANa/TX100, some PANa/TX100/DTAB compounds aggregate to form the flocculates suspending in the solution, and some of them appear at the bottom of the bottle (see the bottle E in Figure 2d); while for TX100/DTAB titrated into PANa, the polymer solution becomes very viscous and solid residues adhere to the bottom of the sample bottle (see the bottle E in Figure 3d). These different phenomena may be explained as follows. The relative amount of TX100 is much less in "Type II" titration than that in "Type I"; thus less DTAB forms free mixed micelles with TX100 in the solution phase and more DTAB interacts with the polymer chains to neutralize the opposite charge density on the polymer chains and more significantly induces polymer cross-linking in "Type II" than that in "Type I". It results the higher viscosity in the "Type II" titration. Further addition of surfactant, the binding curve merges with the background one at C_2, which represents the condition where the polymer chains are completely saturated with surfactants. The binding mechanism and the structure change of polymer/surfactant complex are illustrated in the Figure 4. All the critical concentrations determined by above two titration methods together with the result of titration of DTAB into PANa without TX100[36] are list in Tables 2 and 3, respectively.

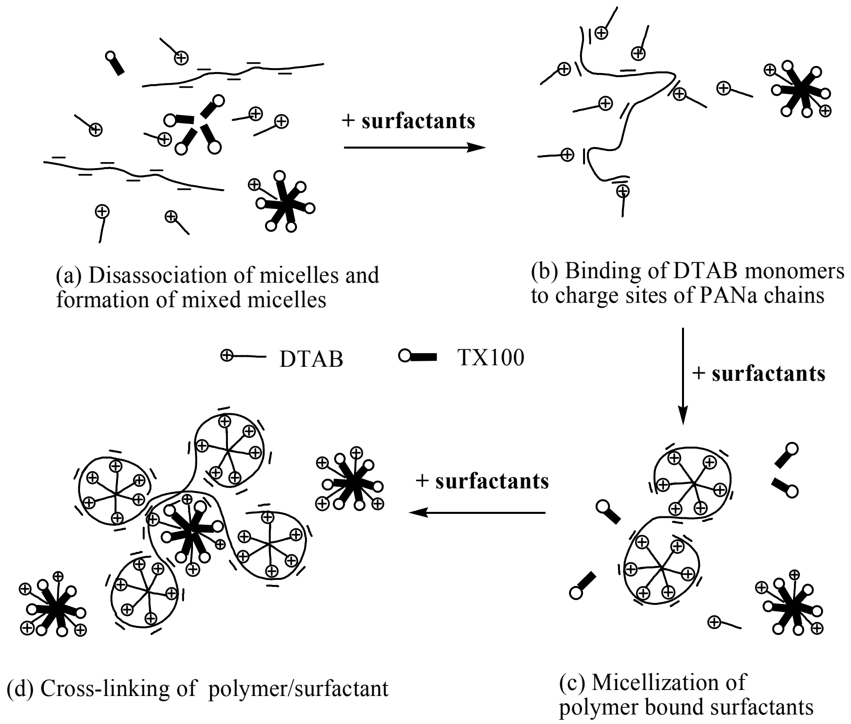

Figure 4. Illustration of interaction mechanism and structure changes of polymer/surfactant complex during the titrations.

Table 2. Critical concentrations for titrating DTAB into PANa/TX100 solutions with various TX100 concentrations

C^0_{TX100} (mM)	C_1 (mM DTAB)	C' (mM DTAB)	C'' (mM DTAB)	$C_{\max}$ (mM DTAB)	C_2 (mM DTAB)
0	0.63	4.72	7.16	7.62	9.32
5.6	0.94	4.17	8.80	9.56	10.95
14.0	1.58	5.27	10.71	12.05	14.54
28.0	2.76	7.54	12.52	13.53	16.09

Table 3. Critical concentrations for titrating TX100/DTAB mixed micelles into PANa solution

C_{TX100}:C_{DTAB}	C_1 (mM surf)	C' (mM surf)	C'' (mM surf)	$C_{\max}$ (mM surf)	C_2 (mM surf)
5.6:70	0.67	2.32	7.95	8.50	9.56
14:70	0.75	3.98	10.62	10.91	12.32
28:70	0.84	5.22	12.21	13.39	15.60

As indicated in Tables 2 and 3, all the critical concentrations increase with the concentration of TX100, since more DTAB monomers are need to participate in the free mixed micelles with TX100 before DTAB monomers bind to negatively charged carboxylate sites along the polymer chains, form the micelles and induce the polymer cross-linking; thus more surfactants are required to reach the corresponding critical conditions.

Peak A indicating DTAB monomers binding to PANa chains through electrostatic interaction and peak B representing the micellization surfactants induced by polymer are endothermic, which are consistent with that of PANa/AOT/DTAB system;[36] however, peaks C of DTAB titrated into PANa/TX100 and TX100/DTAB titrated into PANa are also endothermic, different from those of PANa/AOT/DTAB system; which showed an exothermic peak,[36] indicating that the enthalpy caused by cross linking is system dependent.

It is interesting to compare the "type II" titration results of PANa/TX100/DTAB in this work with that of PANa/AOT/DTAB reported in the previous publication.[36] It was found that when the mixed micelles TX100/DTAB titrated into the polymer solution, the micelles dissociated first, then individual DTAB monomers bound to the polymer; while when the mixed micelles AOT/DTAB titrated into the polymer solution, the mixed micelles were capable to bind into the polymer. It may be explained as follows. Because TX100 has much lower cmc value as compared with AOT, at our experimental conditions and in low surfactant concentration regions, DTAB-rich AOT/DTAB mixed micelle and TX100-rich TX100/DTAB mixed micelle are respectively existed in the corresponding systems. The electrostatic interaction attracts DTAB-rich AOT/DTAB mixed micelles to bind onto PANa chains; moreover, the high hydrophobicity of AOT possibly also reinforces this binding through the hydrophobic interaction. On the other hand, the relative amount of DTAB in the TX100-rich TX100/DTAB mixed micelle is small; hence the charge density of the micelle is too low to be attracted onto the polymer chains.

3.2.3. Thermodynamic characterization of polymer/surfactant interactions

A pseudo phase model[36] was used to analyze the experimental results obtained from "type I" titration to further understand how the concentration of TX100 affects the interactions in PANa/TX100/DTAB system. Before the concentration of DTAB reaches point C_1, there exists an equilibrium of DTAB between aqueous solution phase and TX100/DTAB mixed micelle phase, this equilibrium can be thermodynamically characterized by

$$\mu_{\mathrm{DTAB}}^{\mathrm{aq}} = \mu_{\mathrm{DTAB}}^{\mathrm{mic}} \qquad (2)$$

where $\mu_{\mathrm{DTAB}}^{\mathrm{aq}}$ and $\mu_{\mathrm{DTAB}}^{\mathrm{mic}}$ are the chemical potentials of DTAB in the bulk aqueous solution and in the TX100/DTAB mixed micelles, respectively. These two chemical potentials are expressed by

$$\mu_{\mathrm{DTAB}}^{\mathrm{aq}} = \mu_{\mathrm{DTAB}}^{\mathrm{aq}*} + RT\ln\frac{C_{\mathrm{DTAB}}^{\mathrm{aq}}}{S} \qquad (3)$$

$$\mu_{\mathrm{DTAB}}^{\mathrm{mic}} = \mu_{\mathrm{DTAB}}^{\mathrm{mic}*} + RT\ln\frac{C_{\mathrm{DTAB}}^{\mathrm{mic}}}{C_{\mathrm{TX100}}^{\mathrm{mic}}} \qquad (4)$$

where $\mu_{\mathrm{DTAB}}^{\mathrm{aq}*}$ and $\mu_{\mathrm{DTAB}}^{\mathrm{mic}*}$ are the chemical potentials when the concentration variables $C_{\mathrm{DTAB}}^{\mathrm{aq}}/S$ and $C_{\mathrm{DTAB}}^{\mathrm{mic}}/C_{\mathrm{TX100}}^{\mathrm{mic}}$ equal to 1 and DTAB in the bulk solution and in the surfactant mixture is assumed to have the behavior in an ideal dilute solution; $C_{\mathrm{DTAB}}^{\mathrm{aq}}$, $C_{\mathrm{DTAB}}^{\mathrm{mic}}$ and $C_{\mathrm{TX100}}^{\mathrm{mic}}$ are the concentrations of DTAB in the aqueous solution phase, in the micelle phase and TX100 in the micelle phase, respectively; S =1 mM is used to normalize the concentration $C_{\mathrm{DTAB}}^{\mathrm{aq}}$. As shown in Figure 1, no interaction between TX100 and polymer was detected, thus TX100 only exists in aqueous solution and micelle phases. Because the cmc of the mixed micelles is very low, we neglected the existence of the TX100 monomers in the water phase. Therefore the concentration of TX100 in the micelle phase $C_{\mathrm{TX100}}^{\mathrm{mic}}$ can be substituted by the total concentration of TX100 (C_{TX100}) in the system. Combination of Eqs. (2)-(4) gives

$$K_1 = \frac{C_{\mathrm{DTAB}}^{\mathrm{mic}} / C_{\mathrm{TX100}}}{C_{\mathrm{DTAB}}^{\mathrm{aq}} / S} = \exp[\frac{\mu_{\mathrm{DTAB}}^{\mathrm{aq*}} - \mu_{\mathrm{DTAB}}^{\mathrm{mic*}}}{R\mathrm{T}}] \qquad (5)$$

where K_1 is the equilibrium constant for the equilibrium of DTAB between aqueous phase and TX100/DTAB mixed micelle phase, thus $C_{\mathrm{DTAB}}^{\mathrm{mic}}$ is expressed by

$$C_{\mathrm{DTAB}}^{\mathrm{mic}} = K_1 C_{\mathrm{TX100}} C_{\mathrm{DTAB}}^{\mathrm{aq}} / S \qquad (6)$$

The total concentration of DTAB (C_{DTAB}) in the system can be written as

$$C_{\mathrm{DTAB}} = C_{\mathrm{DTAB}}^{\mathrm{aq}} + C_{\mathrm{DTAB}}^{\mathrm{mic}} = C_{\mathrm{DTAB}}^{\mathrm{aq}} + K_1 C_{\mathrm{TX100}} C_{\mathrm{DTAB}}^{\mathrm{aq}} / S \qquad (7)$$

Assuming that as the concentration of DTAB in the aqueous solution phase reaches a certain value at point C_1, the binding of DTAB monomers to the polymer immediately occurs. When the total concentration of DTAB is above C_1, an amount of DTAB bound to the polymer; thus an additional equilibrium exists in the system, and the phase equilibriums can be characterized by

$$\mu_{\mathrm{DTAB}}^{\mathrm{poly}} = \mu_{\mathrm{DTAB}}^{\mathrm{aq}} = \mu_{\mathrm{DTAB}}^{\mathrm{mic}} \qquad (8)$$

with $\mu_{\mathrm{DTAB}}^{\mathrm{poly}} = \mu_{\mathrm{DTAB}}^{\mathrm{poly*}} + RT \ln \frac{C_{\mathrm{DTAB}}^{\mathrm{poly}}}{C_{\mathrm{poly}}}$ (9)

where $\mu_{\mathrm{DTAB}}^{\mathrm{poly}}$ is the chemical potential of DTAB bound on the polymer, $\mu_{\mathrm{DTAB}}^{\mathrm{poly*}}$ is the chemical potential when the concentration variable $C_{\mathrm{DTAB}}^{\mathrm{poly}} / C_{\mathrm{poly}}$ equals to 1 and the DTAB on the polymer surface has the behavior in an ideal dilute solution, $C_{\mathrm{DTAB}}^{\mathrm{poly}}$ and C_{poly} are the concentrations of DTAB bound on the polymer and the carboxylate groups of the polymer in the system, respectively. Substituting Eqs. (4) and (9) into Eq. (8) gives

$$K_2 = \frac{C_{\mathrm{DTAB}}^{\mathrm{mic}} \big/ C_{\mathrm{TX100}}}{C_{\mathrm{DTAB}}^{\mathrm{poly}} \big/ C_{\mathrm{poly}}} = \exp[\frac{\mu_{\mathrm{DTAB}}^{\mathrm{poly*}} - \mu_{\mathrm{DTAB}}^{\mathrm{mic*}}}{RT}] \qquad (10)$$

with K_2 being the equilibrium constant for the equilibrium of DTAB between TX100/DTAB mixed micelle phase and polymer phase, and thus

$$C_{\mathrm{DTAB}}^{\mathrm{mic}} = K_2 C_{\mathrm{TX100}} C_{\mathrm{DTAB}}^{\mathrm{poly}} \big/ C_{\mathrm{poly}} \qquad (11)$$

The total concentration of DTAB in the system can be written as

$$C_{\mathrm{DTAB}} = C_{\mathrm{DTAB}}^{\mathrm{aq}} + C_{\mathrm{DTAB}}^{\mathrm{poly}} + C_{\mathrm{DTAB}}^{\mathrm{mic}} = C_{\mathrm{DTAB}}^{\mathrm{aq}} + C_{\mathrm{DTAB}}^{\mathrm{poly}} + K_2 C_{\mathrm{TX100}} C_{\mathrm{DTAB}}^{\mathrm{poly}} \big/ C_{\mathrm{poly}} \qquad (12)$$

According to Eq. (7), at point C_1, a plot of C_{DTAB} vs C_{TX100} yields a straight line as shown by line *a* in Figure 5. A linear least-square fit gives Eq. (13)

$$C_{\mathrm{DTAB}} = 0.08 \cdot C_{\mathrm{TX100}} + 0.55 \qquad (13)$$

and then K_1 was calculated to be 0.14 by using the slope and the intercept of Eq. (13). According to Eq. (12), at point C', a plot of C_{DTAB} vs C_{TX100} yields a straight line as shown by line *b* in Figure 5, and a linear least-square fit gives Eq. (14)

$$C_{\mathrm{DTAB}} = 0.13 \cdot C_{\mathrm{TX100}} + 4.06 \qquad (14)$$

The slope $K_2 C_{\mathrm{DTAB}}^{\mathrm{poly}} \big/ C_{\mathrm{poly}}$ and the intercept ($C_{\mathrm{DTAB}}^{\mathrm{aq}} + C_{\mathrm{DTAB}}^{\mathrm{poly}}$) of Eq. (14) were calculated to be 0.13 and 4.16, respectively. Combination of Eqs. (6) and (11) gives $C_{\mathrm{DTAB}}^{\mathrm{aq}} = 0.13 / K_1$; then according to Eq. (12), we have $C_{\mathrm{DTAB}}^{\mathrm{poly}} = 4.16 - C_{\mathrm{DTAB}}^{\mathrm{aq}}$ and $K_2 = 0.13 C_{\mathrm{poly}} / C_{\mathrm{DTAB}}^{\mathrm{poly}}$. It allowed us to calculate $C_{\mathrm{DTAB}}^{\mathrm{poly}} / C_{\mathrm{poly}}$ and K_2 at C', which were 0.49 and 0.26, respectively. The former represents that when the ratio of the concentration of DTAB bound on polymer to the concentration of carboxylate groups reaches 0.49, the formation of polymer induced micelles occur. Also according to Eq.

(12), at points C'', $C_{\max}$ and C_2, plots of C_{DTAB} vs C_{TX100} yield three straight lines as shown by lines *c*, *d* and *e* in Figure 5, and linear least-square fits give Eqs. (15)- (17).

C'': $C_{\mathrm{DTAB}} = 0.23 \cdot C_{\mathrm{TX100}} + 7.54$ (15)

$C_{\max}$: $C_{\mathrm{DTAB}} = 0.26 \cdot C_{\mathrm{TX100}} + 8.16$ (16)

C_2: $C_{\mathrm{DTAB}} = 0.32 \cdot C_{\mathrm{TX100}} + 9.71$ (17)

with the slopes and intercepts of Eqs. (15)-(17) and the calculation procedure used in calculation at point C', the values of $C_{\mathrm{DTAB}}^{\mathrm{poly}}/C_{\mathrm{poly}}$ and K_2 at the three critical points were also obtained. The calculation results of $C_{\mathrm{DTAB}}^{\mathrm{aq}}$, $C_{\mathrm{DTAB}}^{\mathrm{poly}}$, $C_{\mathrm{DTAB}}^{\mathrm{poly}}/C_{\mathrm{poly}}$, K_1, and K_2 at different critical points are listed in Table 4. Finally, according to Eq. (12), the values of $C_{\mathrm{DTAB}}^{\mathrm{mic}}$ at all critical points for different TX100 concentrations were calculated and are summarized in Table 5.

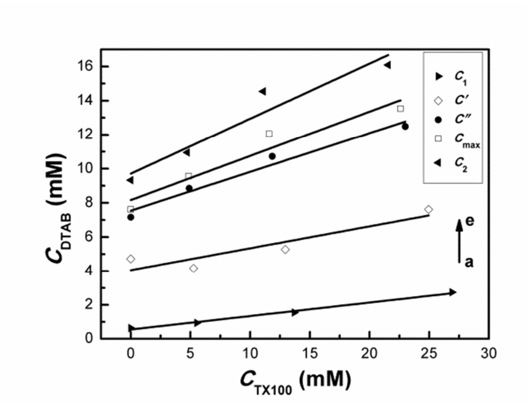

Figure 5. Plots of C_{DTAB} vs. C_{TX100} at critical points C_1, C', C'', $C_{\max}$, C_2. The symbols are the experimental results, and the lines represent the least-squares fits.

As shown in Table 4, the ratios of $C_{\mathrm{DTAB}}^{\mathrm{poly}}\big/C_{\mathrm{poly}}$ increase in the titration process; while K_2 is confirmed to be a constant independent on the concentrations in the system and the amount of DTAB bound to polymer. The ratio of $C_{\mathrm{DTAB}}^{\mathrm{poly}}\big/C_{\mathrm{poly}}$

characterizes the extent of the neutralization of the opposite charges on the polymer. We calculated the value of $C_{\mathrm{DTAB}}^{\mathrm{poly}}/C_{\mathrm{poly}}$ at C'', which was 0.99; however, the ratios of the total DTAB concentration to the carboxylate groups concentration were found to be 1.59, 2.09, and 2.41 for the systems containing TX100 of 5.6 mM, 14 mM and 28 mM, respectively. It confirms that the charge neutralization on the polymer rather than in the whole system decides the cross-linking of the polymer chains.[36] At C_2 the polymer chains are completely saturated with surfactant, and $C_{\mathrm{DTAB}}^{\mathrm{poly}}/C_{\mathrm{poly}}$ equals to 1.3, indicating that charge ratio reverses. At this point redissolution of precipitation was observed although this process is very slow. From Table 5, it is found that for the same critical point, the values of $C_{\mathrm{DTAB}}^{\mathrm{mic}}$ increases with TX100 concentration, indicating that more DTAB participates in the free mixed micelles with TX100 in the solution phase of the system.

Table 4. Values of $C_{\mathrm{DTAB}}^{\mathrm{aq}}$, $C_{\mathrm{DTAB}}^{\mathrm{poly}}$, $C_{\mathrm{DTAB}}^{\mathrm{poly}}/C_{\mathrm{poly}}$, K_1, and K_2 at critical points C_1, C', C'', C_{max} and C_2 calculated by the pseudophase model for DTAB titrated into PANa/TX100 aqueous solutions.

critical points	$C_{\mathrm{DTAB}}^{\mathrm{aq}}$ (mM)	$C_{\mathrm{DTAB}}^{\mathrm{poly}}$ (mM)	$C_{\mathrm{DTAB}}^{\mathrm{poly}}/C_{\mathrm{poly}}$	K_1	K_2
C_1	0.55			0.14	
C'	0.89	3.17	0.49		0.26
C''	1.57	5.98	0.99		0.23
C_{max}	1.79	6.37	1.08		0.24

C_2	2.23	7.48	1.31		0.25

Table 5. Values of $C^{\mathrm{mic}}_{\mathrm{DTAB}}$ (mM) at critical points C_1, C', C'', $C_{\max}$ and C_2 for DTAB titrated into PANa/TX100 aqueous solutions with various TX100 concentrations C^0_{TX100}.

critical points	$C^{\mathrm{mic}}_{\mathrm{DTAB}}$ (mM)		
	C^0_{TX100} 5.6	14	28
C_1	0.39	1.00	2.19
C'	0.11	1.21	3.56
C''	1.30	3.17	4.93
$C_{\max}$	1.40	3.89	5.37
C_2	1.24	4.83	6.38

4. Conclusions

Interactions between PANa and TX100/DTAB mixed surfactants in 40 mM NaBr solutions were studied by isothermal titration calorimetry (ITC). It was found that when TX100/DTAB titrated into NaBr solution, TX100-rich mixed micelles formed first, then changed to DTAB-rich mixed micelles. The values of critical concentration cmc_1 of TX100/DTAB mixed micelles were all smaller than that calculated by Clint's equation, suggesting the synergistic effects between TX100 and DTAB.

At low ionic strength (40 mM NaBr), whatever DTAB titrated into PANa/TX100 or TX100/DTAB titrated into PANa, three endothermic peaks were detected; which represented the binding of DTAB monomers to PANa chains through the electrostatic interaction, polymer-induced micellization, and cross-linking of polymer chains, respectively. The sign of the observed differential enthalpy of peak C was found to be opposite to that of the system PANa/AOT/DTAB, which reflected that the enthalpy effect of cross-linking was system dependent. The interaction mechanism was interpreted by a thermodynamic model, through which, it was found that when the mole ratio of bound-DTAB to the carboxylate group of the polymer ($C_{\mathrm{DTAB}}^{\mathrm{poly}}/C_{\mathrm{poly}}$) reached about 0.5, the polymer-induced micellization occurred; when $C_{\mathrm{DTAB}}^{\mathrm{poly}}/C_{\mathrm{poly}}$ reaches about 1, the cross-links of polymer chains started and precipitation was observed, indicating that the charge neutralization on the polymer rather than in the whole system decides the cross-linking of the polymer chains; finally as $C_{\mathrm{DTAB}}^{\mathrm{poly}}\big/C_{\mathrm{poly}}$ reached 1.3, the polymer chains are completely saturated with surfactant, precipitation was redissolved slowly. This study may shed new light on understanding the interaction mechanism of the polyelectrolyte/mixed surfactant system, which would help to design rational polymer/surfactant systems for various applications, however more investigations are required to further validate the proposed mechanism and thermodynamic model.

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